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(54) Title: ANTI-REFLECTIVE COATING

(57) Abstract

The present invention provides a three-layer anti-reflective coating, each layer being made of a combination of materials designed to provide the coating with a desired index of refraction. The invention combines two or more materials to form an alloy whose oxide deposit has anti-reflective properties not found in naturally occurring elements. Each layer is designed to have a specific index of refraction that approximates the relation $n_1n_3/n_2 = \sqrt{(n_sn_0)}$ wherein n_1, n_2 and n_3, respectively, represent the refractive indices of the first, second, and third layers. In this case n_s represents the refractive index of the substrate and n_0 is the refractive index of air. The first and second layers are formed by reactively sputtering metal alloys in the presence of oxygen to obtain oxide deposits having a predetermined index of refraction. The oxide deposits may be applied to the substrate by physical vapor deposition methods.

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ANTI-REFLECTIVE COATING

BACKGROUND

1. Introduction

This invention relates to a three layer anti-reflective coating applied to optical lenses and other transparent substrates. More particularly, the invention relates to an anti-reflective coating which uses alloy targets specifically fabricated to produce coating layers having a desired index of refraction.

2. Description of the Prior Art

Three layer coatings intended to provide some degree of anti-reflection are known in the art. For example, U.S. Pat. No. 5,372,874, and the cited references disclose the use of three layer anti-reflection coating systems. The layers of the anti-reflective coating generally comprise oxides of various elements deposited on the surface of a substrate by known techniques. The deposition techniques can include physical vapor deposition techniques such as ablation, evaporation, and reactive and non-reactive sputtering.

The use of metal oxides and oxides of metal alloys in prior art anti-reflective coatings is known. For example, U.S. Pat.

No. 5,372,874 discloses the use of metal oxides in a three layer system, and U.S. Pat. Nos. 5,216,542 and 5,279,722 disclose the use of oxides of metal alloys such as nickel-chromium and tin-ytterbium in four, five, and six layer anti-reflective coating systems. The present invention concerns the development of a more efficient three layer anti-reflective coating.

In theory, a perfectly anti-reflecting three layer coating can be applied to an optical element such that the thicknesses of the first, second and third layers respectively satisfy the relationship

$$\lambda/4 | \ \lambda/2 | \ \lambda/4 \qquad \text{(Equation 1)}$$

where λ is the wavelength desired to be non-reflecting. The indices of refraction for the layers of the coating satisfy the condition

$$n_1 n_3/n_2 = \sqrt{(n_S \, n_O)} \qquad \text{(Equation 2)}$$

where n_1, n_2, and n_3 are the refractive indices of the respective layers, and n_0 is the refractive index of air. There, however, are no naturally existing materials having refractive indices which satisfy the equality of Equation (2).

Various solutions are disclosed in the prior art to overcome this problem. Such solutions include substituting two or more layers for one of the three layers in the coating to approximate the desired refractive indices. In other words, indices of refraction that do not exist in available materials

are simulated by combining two or more separate layers of materials such that the average of their indices approximates a desired index of refraction.

Using two or more layers to simulate a desired index of refraction has a number of disadvantages. First, because the layers in an optical coating are relatively thin, manufacturing is complicated by the addition of layers, making quality control difficult. Second, normal production variations can cause deviations in the physical thickness of the layers, resulting in material changes in their index of refraction. Consequently, there exists a need to provide a material having a precise index of refraction that can approximate the relation of Equation (2) using a three layer coating.

It is therefore an object of the present invention to form a coating system having an index of refraction which approximates the equality of Equation (2).

It is another object of this invention to provide an alloy for use in an anti-reflective coating wherein the alloy has a refractive index equal to the resultant contribution of the refractive indices of the elements forming the alloy.

A further object of this invention is to provide for simplified manufacturing of optical lenses having an anti-reflective coating.

These and other objects of this invention will be better understood by reference to the following description, drawings, and claims.

SUMMARY OF THE INVENTION

The present invention provides a three-layer anti-reflective coating for an optical lens. The anti-reflective coating also can be used on camera or telescope lenses, automobile or building windows, television viewing surfaces, or other optically functional structures. Each coating layer is made of a combination of materials designed to provide the coating with a desired index of refraction. The invention combines two or more materials to form an alloy whose oxide deposit has anti-reflective properties not found in naturally occurring elements. For example, the invention permits the combination of two or more metals to form an alloy. The oxide of the alloy approximates an index of refraction that does not exist in known elements.

Specifically, the invention relates to an anti-reflective coating which includes a three layer stack deposited onto a substrate. Each layer is designed to have a specific index of refraction that approximates the relation of Equation (2):

$$n_1 n_3 / n_2 = \sqrt{(n_s n_0)}$$

wherein n_1, n_2, and n_3, respectively, represent the refractive indices of the first, second, and third layers, n_s represents the refractive index of the substrate, and n_0 is the refractive index of air. The first and second layers are formed by reactively sputtering metal alloys in the presence of oxygen to obtain

oxide deposits having a predetermined index of refraction. The oxide deposits may be applied to the substrate by physical vapor deposition methods. The third layer may be formed by reactive sputtering or by other methods. Any one of the three layers may be preselected, such that the other two layers are chosen based on the preselected layer.

The process of making the three stack (layer) anti-reflective coating, such that its anti-reflective properties approximate the relationship of Equation (2), includes selecting a substrate having a determinable index of refraction (n_s). A first coating layer is deposited on the substrate. If the third layer is the preselected layer, then the first coating layer, comprising an oxide deposit formed by reactively sputtering a metal alloy, is specifically designed to provide the oxide with a refractive index which approximates the relationship

$$n_1 = \sqrt{n_s} \times n_3 \qquad \text{(Equation 3)}$$

wherein n_s is the refractive index of the substrate and n_3 represents the refractive index of a third coating layer.

A second coating layer is deposited onto the first layer using physical vapor deposition techniques. For example, the second layer can be reactively sputtered onto the first coating layer using a specially designed metal alloy target. Again, if the third layer is the preselected layer, the metal alloy for the second layer is fabricated to provide an oxide deposit having a refractive index (n_2) which approximates the relation

$$n_2 = (n_3)^2 \qquad \text{(Equation 4)}$$

wherein n_3 represents the refractive index of the third layer.

Finally, a third coating layer is deposited on the second layer by physical vapor deposition techniques. The third layer in this example has a known index of refraction (n_3), and can comprise boron-doped silicon dioxide reactively sputtered onto the second layer. Similarly, another three layer stack may be deposited on the opposite interface of the substrate to eliminate reflection from that interface also.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of a three layer coating formed in accordance with the teachings of this invention and applied to a substrate.

Figures 2(a-b) are X-ray photoelectron spectroscopy (XPS) scans of titanium reactively sputtered with oxygen from a pure titanium target, and titanium reactively sputtered with oxygen from an alloy target comprising titanium and aluminum.

Figures 3(a-b) are XPS scans for aluminum reactively sputtered with oxygen from a pure aluminum target, and aluminum reactively sputtered with oxygen from an alloy target comprising aluminum and titanium.

Figures 4(a-c) are XPS scans of oxygen peaks from reactively sputtered layers of pure titanium, pure aluminum, and an alloy target comprising titanium and aluminum.

Figures 5(a-c) are XPS scans of carbon contaminants that exist in sputtered deposits of aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), and an oxide sputtered from an alloy of titanium mixed with aluminum.

DETAILED DESCRIPTION

This invention relates to a process of forming and applying an anti-reflection coating to transparent or nontransparent substrates, and the formation of alloys for use in the coating system. The substrate can include an optical, camera, or telescope lens; automobile or building windows; television viewing surfaces; or other optically similar structures. To reduce the reflective properties of the substrate, it is coated with an anti-reflective coating having a precise index of refraction.

The coating includes three layers. The first coating layer is deposited directly on the surface of the substrate. The second layer is deposited on the first layer, and the third layer is deposited on the second layer. The first and second layers preferably are formed by separately depositing oxides of specially designed metal alloys on the substrate. The alloys are custom designed such that their oxides provide an index of refraction which does not exist in naturally occurring elements. While the third layer preferably is formed of a material having a known index of refraction, any one of the three layers may be preselected such that the other two layers are chosen based on the preselected layer. The third layer can have a low index of refraction and hardness and corrosion resistant properties. The layers can be arranged in any order, and are not intended to be limited to the above description. In addition, another three layer stack of the invention may be deposited on the opposite

interface of the substrate to eliminate reflection from that interface.

The layers of the anti-reflective coating can be applied to the substrate using commonly known physical vapor deposition techniques such as ablation, evaporation, reactive and non-reactive sputtering, or other similar methods.

To select the desired index of refraction for each coating layer, the theoretical calculation for zero reflection is performed. The calculation is performed using the substrate's refractive index and that of a chosen material whose index is known. This fixes or limits the indices of refraction for the other two layers in accordance with the following equation:

$$r_{eq1} = \frac{r_1 - r_2 \ exp.(-i\delta_1)}{1 - r_1 r_2 \ exp.(-i\delta_1)} \qquad \text{(Equation 5)}$$

$$\approx r_1 - r_2 \ exp.(-I\delta_1)$$

$$r_{eq2} \approx r_3 - r_4 \ exp.(-I\delta_3)$$

now if

$$r_1 = r_2 = r_3 = r_4 \text{ and}$$

$$exp.(-i\delta_1) = exp.(-i\delta_2) = 1 (od_1 = od_3 = \lambda_1/4)$$

then

$$r_{eq1} = r_{eq2} = 0$$

so that

$$r_{eq.total} = 0$$

This condition is satisfied when:

$$n_2 = (n_3)^2 \qquad \text{(Equation 4)}$$

and

$$n_1 = \sqrt{n_s} \times n_3 \qquad \text{(Equation 3)}$$

where n_1, n_2, and n_3 are the refractive indices of the first, second, and third layers, respectively, and n_s is the refractive index of the chosen substrate. In accordance with the invention, any index of refraction between the lowest and highest naturally available elements (elements having an index of refraction between 1.38-2.9) can be achieved by fabricating a metal alloy target. The metal alloy target is designed to produce an oxide deposit having an index of refraction that is the resultant contribution of the refractive index of each element forming the alloy.

To fit the formula, any combination of metals that produce a clear oxide, fluoride, or nitride can be used. As a general rule, an alloy is produced from materials with higher and lower indices than the desired resultant index. However, the resultant index is not a straight average of the two numbers, and before selecting an alloy, the sputtering rate of each element in the alloy target and of the oxide formed from the elements must be taken into consideration.

The drawings show the formation and properties of an anti-reflective coating of the present invention. Figure 1 is a cross-sectional view of an embodiment of a three layer coating 10 applied to a substrate 12 in accordance with this invention. The substrate 12 is an optical lens having an index of refraction (n_s) of 1.5. As previously discussed, the substrate 12 need not be limited to an optical lens, and may include any substrate onto which an anti-reflective coating is applied, such

as glass, polycarbonate, or other materials. The substrate 12 includes a front side 14 that faces an observer having a line of sight through the substrate 12 as shown. An anti-reflective coating 10 is deposited on the front side 14 of the substrate 12.

The anti-reflective coating 10 includes three layers: a first layer 16 deposited directly onto the front surface 14 of the substrate 12; a second layer 18 formed directly on the first layer 16; and a third layer 20 formed on the second layer 18. In a preferred embodiment, the index of refraction of each layer 16, 18, and 20 is determined by Equations (3) and (4) such that the indices of refraction approximate the relationship of Equation (2).

Using the relationship of Equation (2), if the material forming the third layer 20 is preselected, the index of refraction (n_3) of the third layer 20 is established as a known value. Consequently, the index of refraction of the first and second layers 16 and 18 is fixed by n_3 and n_s, where n_s is known. An example of a three layer coating of the present invention, designed based on a preselected third layer, follows.

EXAMPLE

In a preferred embodiment, the third layer 20 is boron-doped silicon dioxide (SiO_2), which has an index of refraction, n_3, of 1.502 measured at 550 nm. The index of refraction, n_2, of

the second layer 18 is therefore determined using Equation (4) such that

$$n_2 = (n_3)^2 = (1.502)^2 = 2.256.$$

The refractive index (n_1) of the first layer 20 is established using Equation (3):

$$n_1 = \sqrt{n_s} \times n_3 = \sqrt{1.5} \times 1.502 = 1.840.$$

Various alloys may be chosen to form the layers 16 and 18 such that the resultant oxides deposited as layers 16 and 18 in a preferred embodiment provide indices of refraction of 1.840 and 2.256, respectively. In the example, the first layer 16 is formed from an aluminum-zinc alloy, 94.35% aluminum and 5.65% zinc, reactively sputtered in the presence of oxygen to produce an oxide deposit having a refractive index of 1.840. The second layer 18 is formed from a titanium-aluminum alloy, 98.27% titanium and 1.73% aluminum, reactively sputtered in the presence of oxygen to provide an oxide deposit with an index of refraction of 2.256.

The preferred method of depositing the coating 10 on the substrate 12 is reactive sputtering. Sputtering is performed with a magnetron in a reactive gas environment composed of a discharge gas comprising argon (Ar) and a reactive gas comprising oxygen. The argon gas is selectively fed into a sputtering gun to reduce oxidation of the target material. The oxygen gas is fed directly into the sputtering chamber.

Sputtering the base or target material in the reactive oxygen gas creates an oxide of the target material on the surface of a substrate placed in the sputtering chamber.

In the above example, the first layer 16 is sputtered onto the substrate 12 using a target comprising an alloy of aluminum and titanium having the composition previously described. The second layer 18 is reactively sputtered using a target alloy comprising titanium and zirconium as described above. The third layer 20 is reactively sputtered onto the second layer 18 using a boron-doped silicon target.

The first, second, and third layers 16, 18, and 20 have an optical thickness (t_o) of $\lambda/4$, $\lambda/2$, and $\lambda/4$ respectively, where λ is approximately 550 nm. The physical thickness of the first, second, and third layers 16, 18, and 20 is determined by the relationship

$$t_p = t_o/n \qquad \text{(Equation 6)}$$

where t_o is the optical thickness and "n" represents the refractive index of the layer. Since the refractive index is a predetermined constant, its value is not affected by small variations in either the physical or optical thicknesses.

Tests on the example coating using X-ray photoelectron spectroscopy (XPS) show that the deposited alloy oxide layers 16 and 18 include compounds other than the separate oxides of the metallic elements forming the alloys. XPS scans are generally performed in a vacuum and require irradiating a solid surface

with x-rays. See generally Perkin-Elmer Corporation, Handbook of X-ray Photoelectron Spectroscopy (1992). An XPS analysis of a compound provides information concerning its binding energy, that is energy required to remove one electron from a solid surface. A unique XPS plot or spectrum exists for all compounds, wherein the binding energy plot of each compound is represented as peaks or inflections in the scan. The XPS plot obtained for layers 16 and 18 is different from that generated by the metal oxides believed to comprise each layer.

For example, XPS scans were performed on deposits of an aluminum-titanium alloy, $Al_{57}Ti_{43}$, a pure aluminum target, and a pure titanium target, all reactively sputtered in the presence of oxygen. The XPS scans of the reactively sputtered aluminum-titanium alloy includes peaks which do not belong to either of the oxides of its constituent metals or the pure elements forming the alloy. These peaks indicate that the oxide of the sputtered alloy contained compounds other than aluminum oxide (Al_2O_3) and titanium oxide (TiO_2).

Figure 2a is an XPS scan of the titanium peak from titanium oxide. The binding energy of the titanium peak is shown as a single peak at 458.35 eV. The published binding energy for titanium in TiO_2 is 458.8 eV. The difference in the binding energies is believed to be due to non-stoichiometry in the deposited film.

Figure 2b is an XPS scan of the titanium peak from the aluminum-titanium oxide sputtering. This scan shows the

titanium element as having peaks at 458.4 and 458.0 eV. The peak at 458.4 eV is consistent with the binding energy of titanium oxide, but the peak at 458.0 eV is not a known binding energy for titanium or titanium oxide. The closest reported binding energy is 458.3 eV, which belongs to the metal titanates group (i.e., $BaTiO_3$, $PbTiO_3$, etc.). This extra peak at 458.0 eV is presumably due to the compounding of the titanium with aluminum and oxygen.

Figure 3a is an XPS scan of the aluminum peak from the aluminum oxide sputtering. The XPS scan shows two peaks, one at 74.0 eV and the other at 73.75 eV. This scan is within the range of published data which reports the binding energy of aluminum in aluminum oxide at about 74.1 eV ± 0.3 eV.

Figure 3b is an XPS of the aluminum peak from the aluminum titanium oxide sputtering. This scan shows a peak at 73.7 eV and an inflection at 73.0 eV. The shift in the binding energy value of the aluminum in the aluminum-titanium oxide deposit is presumably due to the presence of an additional compound other than pure aluminum oxide in the deposit.

Figures 4(a-c) are XPS scans of the respective oxygen peaks from pure titanium, pure aluminum, and the alloy target deposits. Figure 4a shows a scan of the oxygen peak from the titanium oxide (TiO_2) sputtering. The scan shows a peak at approximately 529.4 eV, a value which is consistent with published data.

Figure 4b is an XPS scan of the oxygen peak from the aluminum oxide (Al_2O_3) sputtering. This scan shows peaks at 536.85 eV, 530.45 eV and 530.25 eV. Again, the measured binding energies are consistent with published data.

Figure 4c shows an XPS scan of oxygen from the aluminum titanium oxide sputtering. This scan shows a number of peaks and inflections. For example, the scan shows peaks at 529.65, 530.5, 530.05 and 531.05 eV, and smaller inflections at 528.95, 529.3 and 531.4 eV. The peaks and inflections shown in the sputtered aluminum titanium oxide are not consistent with known data for oxygen in aluminum oxide or titanium oxide. This information suggests the presence of other compounds.

As a precaution, each of the XPS scans were set-up to scan the compositions under analysis for contaminants. Figures 5(a-c) are scans of the carbon contaminants that invariably exist on all surfaces. This scan was used as a marker to show that the XPS scans of the sputtered materials were not shifted in any way by the charging of the samples. Normal hydrocarbons have their carbon peak at 284.8 eV. It is clear from Figures 2-4 that the scans were not shifted.

While the invention has been described in connection with several specific embodiments, it should be understood that numerous modifications in dimensions, materials and/or techniques could be made by persons of ordinary skill in this art without departing from the scope of this invention. Accordingly, the foregoing description is intended to be merely

illustrative and thus not limiting. The scope of the invention as claimed should be understood to include all those alternatives and modifications which the above specification and drawings would suggest, or which would readily occur and/or be apparent to one skilled in the art upon study of the same.

WHAT IS CLAIMED:

1. An anti-reflective coating, comprising a three layer stack deposited onto a substrate, wherein the first layer having an index of refraction n_1 is deposited onto the substrate having an index of refraction n_s, the second layer having an index of refraction n_2 is deposited onto the first layer, the third layer having an index of refraction n_3 is deposited onto the second layer, and the layers are designed such that their indices of refraction approximate the relation $n_1n_3/n_2 = \sqrt{(n_sn_{air})}$.

2. The anti-reflective coating of claim 1 wherein the first and second layers comprise oxide deposits produced by physical vapor deposition.

3. The anti-reflective coating of claim 1 wherein the first and second layers comprise oxide deposits produced by reactively sputtering metal alloy targets in the presence of oxygen.

4. The anti-reflective coating of claim 1 wherein the third layer comprises boron-doped silicon dioxide.

5. An anti-reflective coating, comprising first, second, and third layers, wherein the first layer is deposited on a substrate having a known or determinable index of refraction, and the first layer has an index of refraction approximately equal to the square root of the index of refraction of the

substrate multiplied by the index of refraction of the third layer;

the second layer is deposited on the first layer and has an index of refraction approximately equal to the square of the index of refraction of the third layer; and

the third layer is deposited on the second layer that has a known index of refraction.

6. The anti-reflective coating of claim 5 wherein the third layer comprises boron-doped silicon dioxide.

7. The anti-reflective coating of claim 5 wherein the first and second layers comprise deposits from an alloy target specifically designed to provide an oxide deposit having a specific refractive index.

8. The anti-reflective coating of claim 7 wherein the first and second layers comprise deposits from different alloys, each alloy being specifically designed to provide an oxide deposit having a specific refractive index.

9. The anti-reflective coating of claim 8 wherein each alloy is separately reactively sputtered to form a layer of the coating.

10. The anti-reflective coating of claim 8 wherein the alloy used to form the first layer of the coating comprises a composition of about 94 percent aluminum and about 6 percent zinc.

11. The anti-reflective coating of claim 8 wherein the alloy used to form the second layer of the coating comprises a composition of about 98 percent titanium and about 2 percent aluminum.

12. The anti-reflective coating of claim 8 wherein the alloy used to form the first layer of the coating comprises a composition of about 94 percent aluminum and about 6 percent zinc, and the alloy used to form the second layer of the coating comprises a composition of about 98 percent titanium and about 2 percent aluminum.

13. A process of making a three layer anti-reflective coating wherein each layer is designed to have a specific index of refraction which approximates the relation $n_1 n_3 / n_2 = \sqrt{(n_s n_0)}$, the process comprising the steps of:

providing a substrate having a determinable index of refraction (n_s),

depositing on the substrate by physical vapor deposition techniques a first layer comprising a metal oxide deposit formed by reactively sputtering a metal alloy target to produce the metal oxide deposit with a refractive index (n_1) having an approximate value determined by the relation

$$n_1 = \sqrt{n_s} \times n_3$$

wherein n_s is the refractive index of the substrate and n_3 represents the refractive index of the third layer,

depositing on the first layer by physical vapor deposition techniques a second layer comprising a metal oxide formed by reactively sputtering a metal alloy target specifically designed to produce the metal oxide deposit with a refractive index (n_2) having an approximate value determined by the relation

$$n_2 = (n_3)^2$$

wherein n_3 represents the refractive index of the third layer, and

depositing on the second layer by physical vapor deposition techniques a third layer having a known index of refraction (n_3).

14. The process of claim 13 wherein the first layer has a refractive index of approximately 1.840 and is deposited by reactively sputtering a metal alloy comprising about 94 percent aluminum and about 6 percent zinc in the presence of oxygen.

15. The process of claim 13 wherein the second layer has a refractive index of approximately 2.256 and is deposited by reactively sputtering a metal alloy comprising about 98 percent titanium and about 2 percent aluminum in the presence of oxygen.

16. The process of claim 13 wherein the third layer comprises boron-doped silicon dioxide having a refractive index of approximately 1.502, wherein the silicon dioxide is reactively sputtered onto the second layer.

17. The process of claim 13 wherein the first layer has a refractive index of approximately 1.840 and is deposited by reactively sputtering a metal alloy comprising about 94 percent aluminum and about 6 percent zinc in the presence of oxygen, the second layer has a refractive index of approximately 2.256 and is deposited by reactively sputtering a metal alloy comprising about 98 percent titanium and about 2 percent aluminum in the presence of oxygen, and the third layer comprises boron-doped silicon dioxide having a refractive index of approximately 1.502 and is reactively sputtered onto the second layer.

18. The process of claim 17 wherein the substrate is glass.

19. The process of claim 13 wherein the first layer has a refractive index of approximately 1.90 and is deposited by reactively sputtering a metal alloy comprising about 94 percent aluminum and about 6 percent zinc in the presence of oxygen, the second layer has a refractive index of approximately 2.256 and is deposited by reactively sputtering a metal alloy comprising about 98 percent titanium and about 2 percent aluminum in the presence of oxygen, and the third layer comprises boron-doped silicon dioxide having a refractive index of approximately 1.502 and is reactively sputtered onto the second layer.

20. The process of claim 19 wherein the substrate is polycarbonate.

OBSERVER LINE OF SIGHT

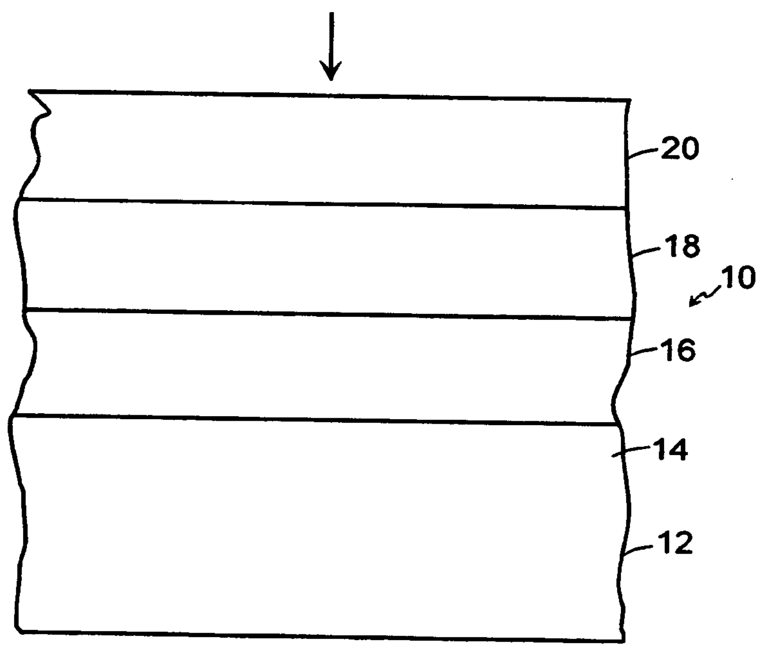
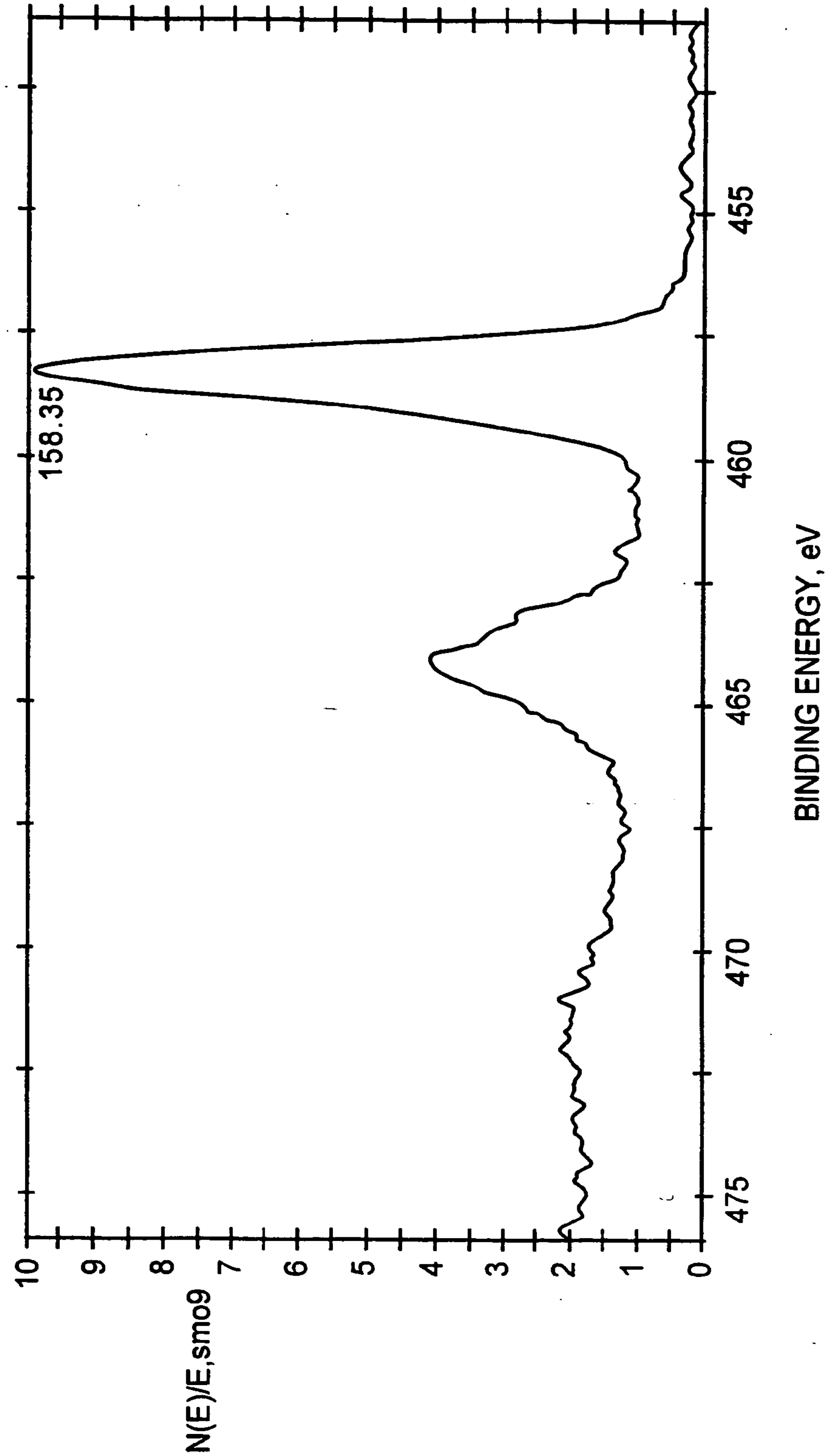


FIG. 1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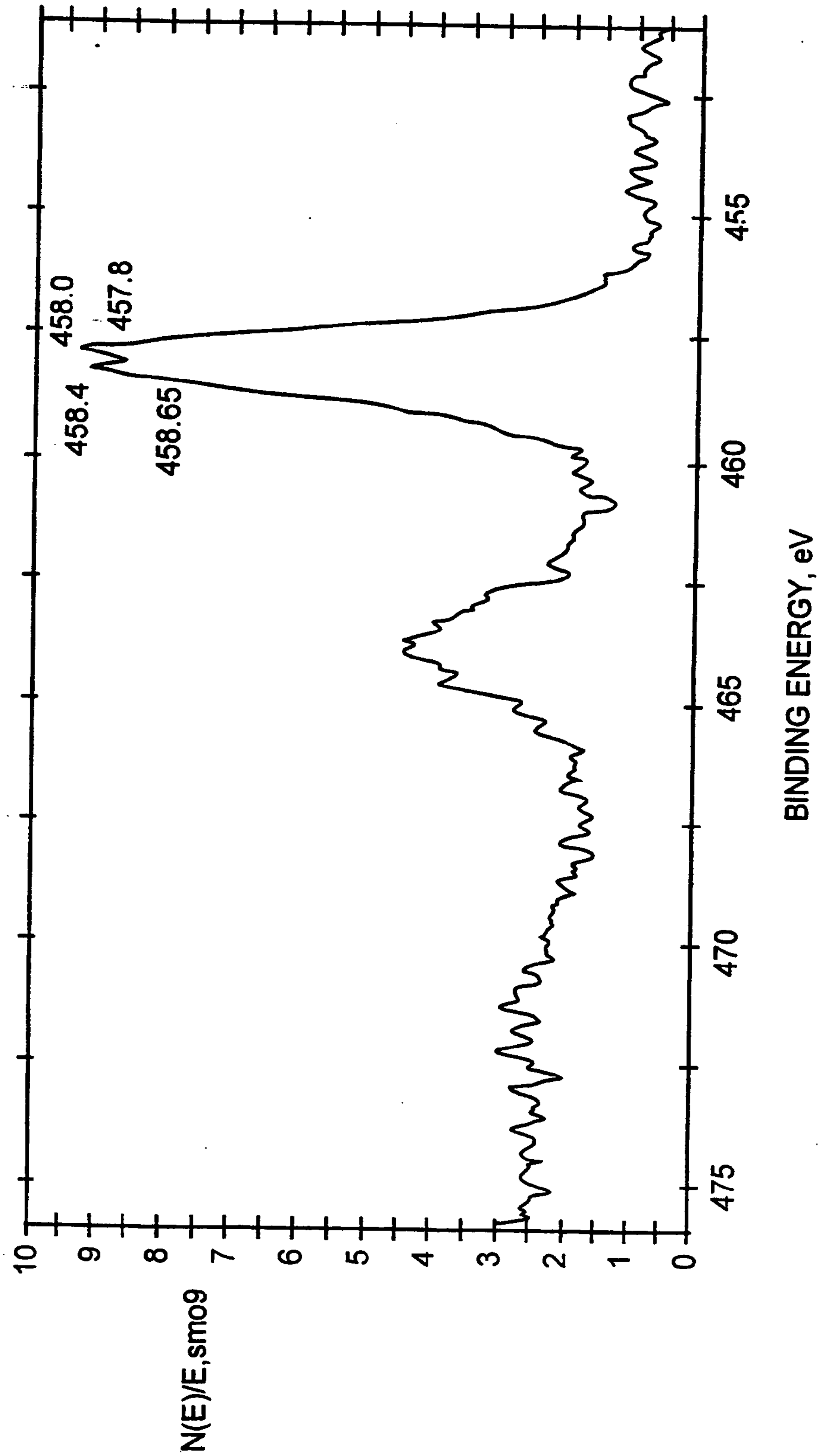
N(E)/E,smo9

FIG. 2a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458.4
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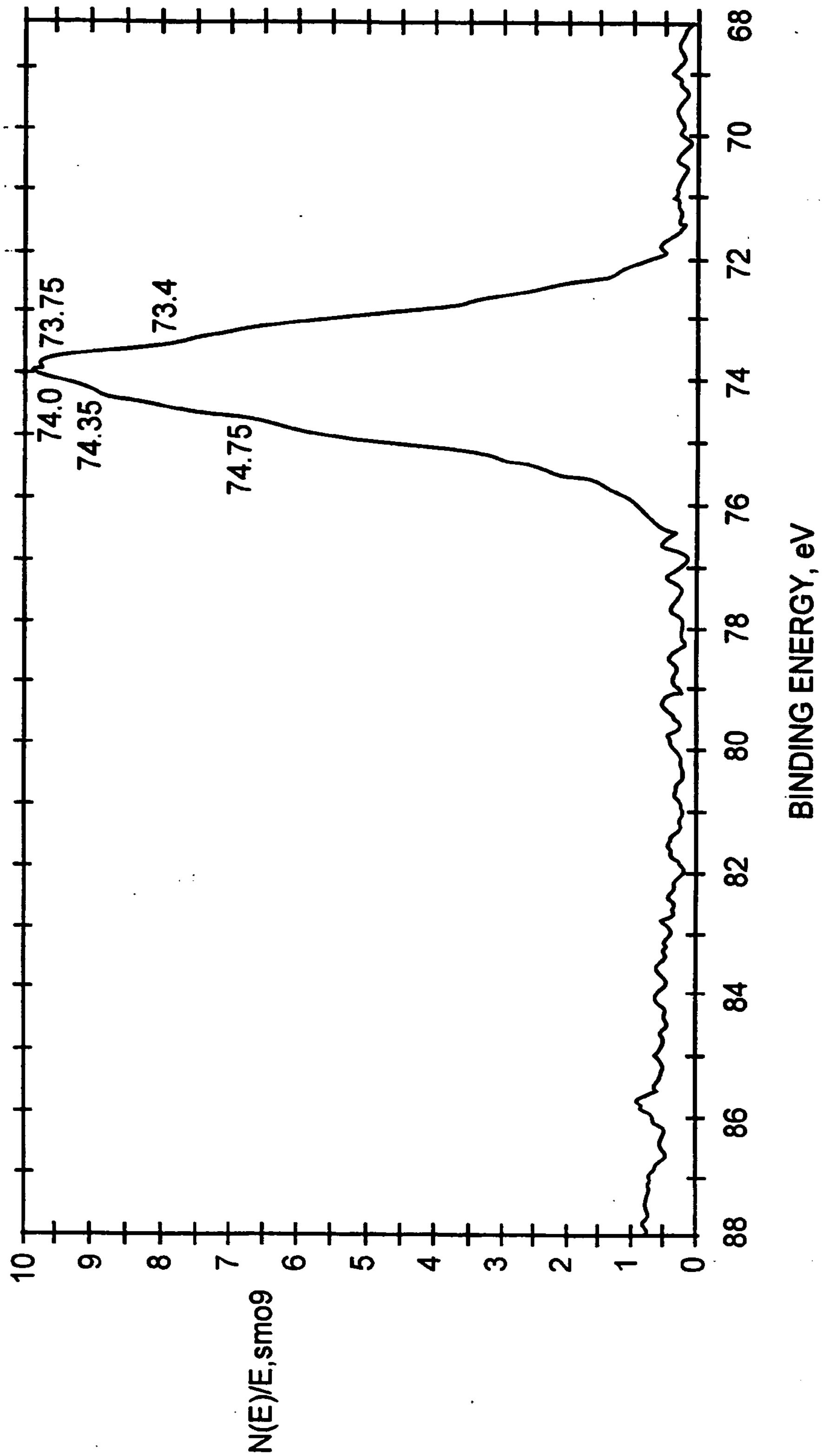
FIG. 2b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73.4
74.0
74.35
74.75
68
70
72
74
76
78
80
82
84
86
88
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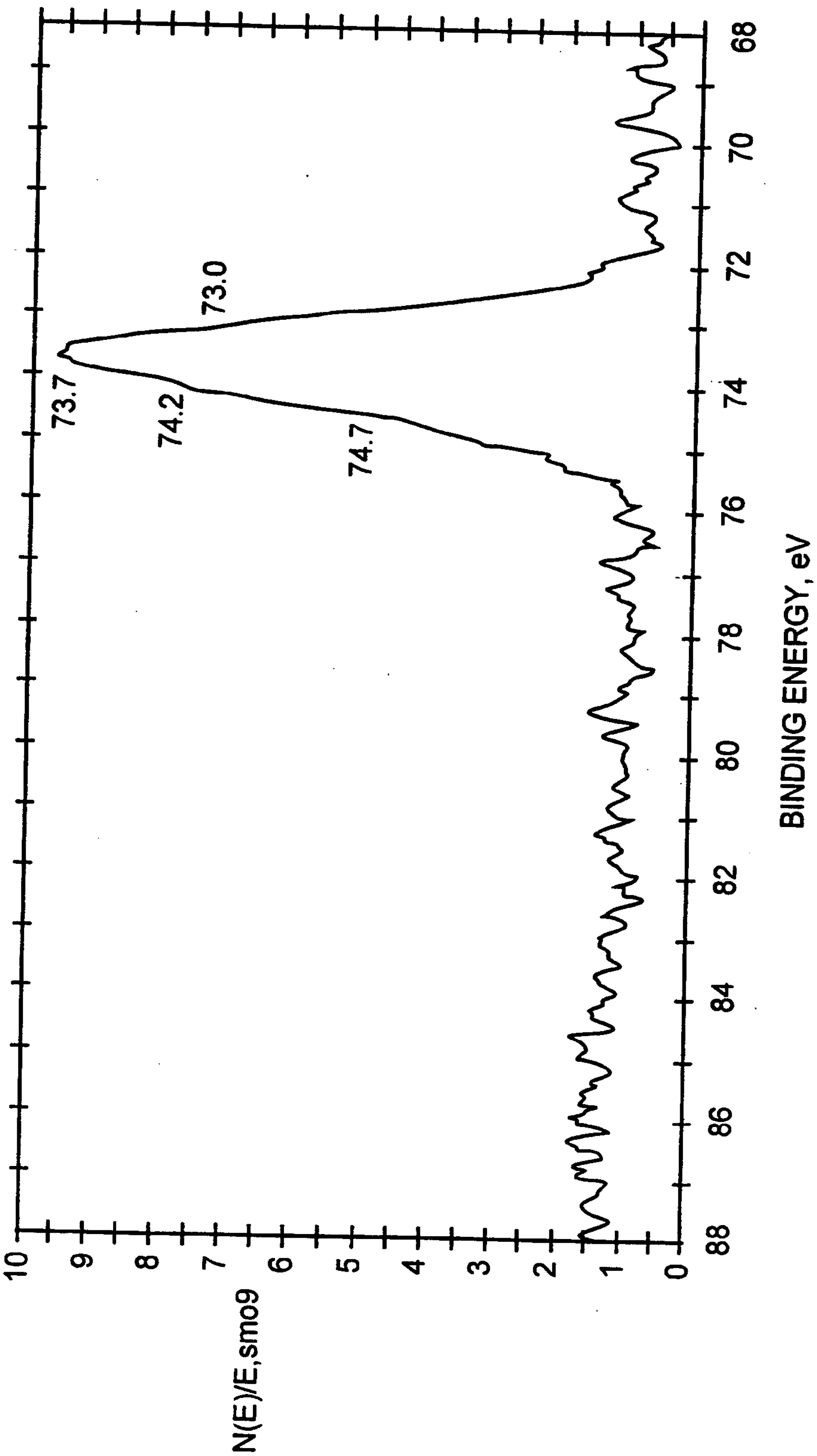
FIG. 3a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BINDING ENERGY, eV
0 1 2 3 4 5 6 7 8 9 10
88 86 84 82 80 78 76 74 72 70 68
73.7
74.2
74.7
73.0

FIG. 3b

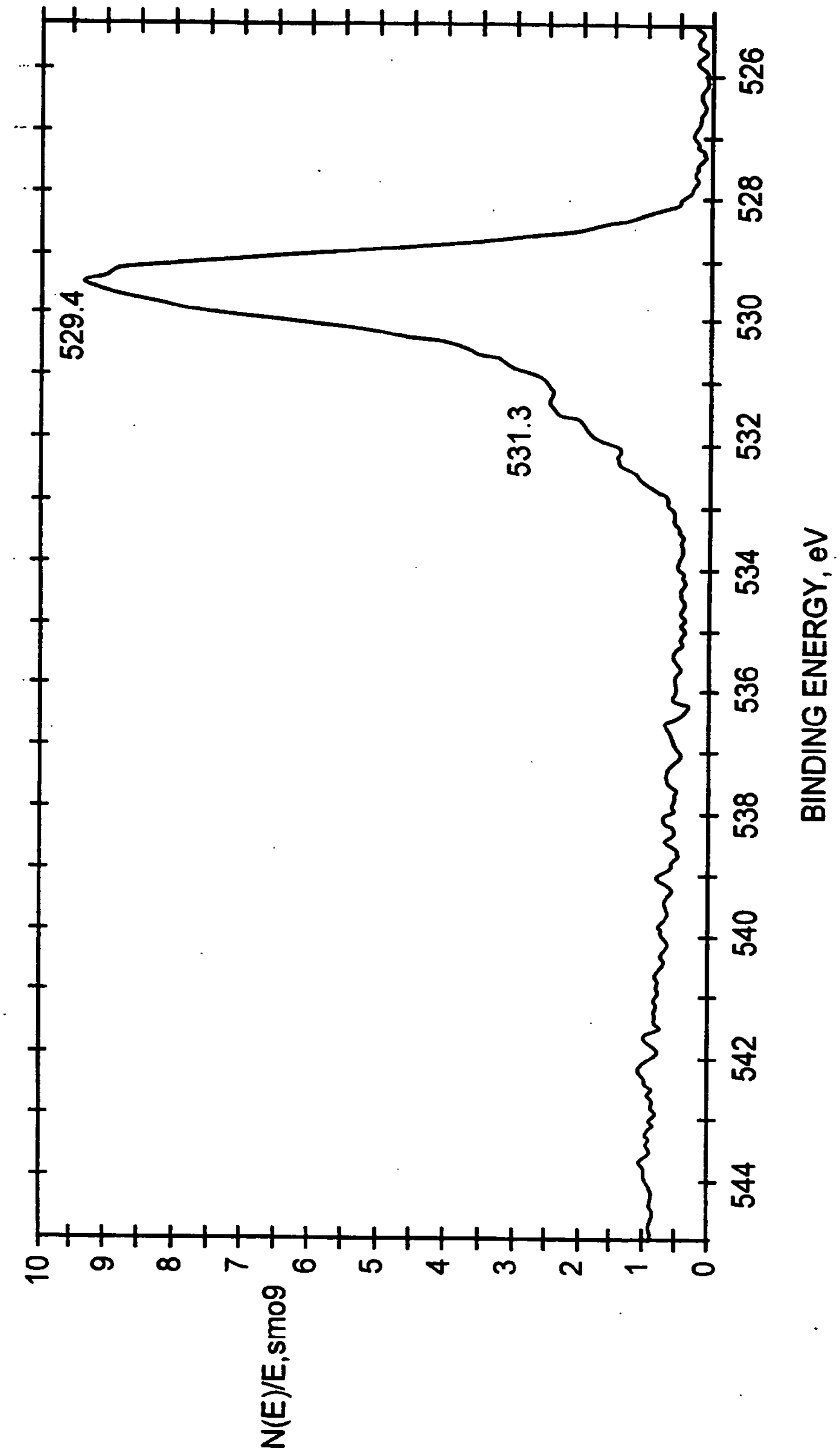
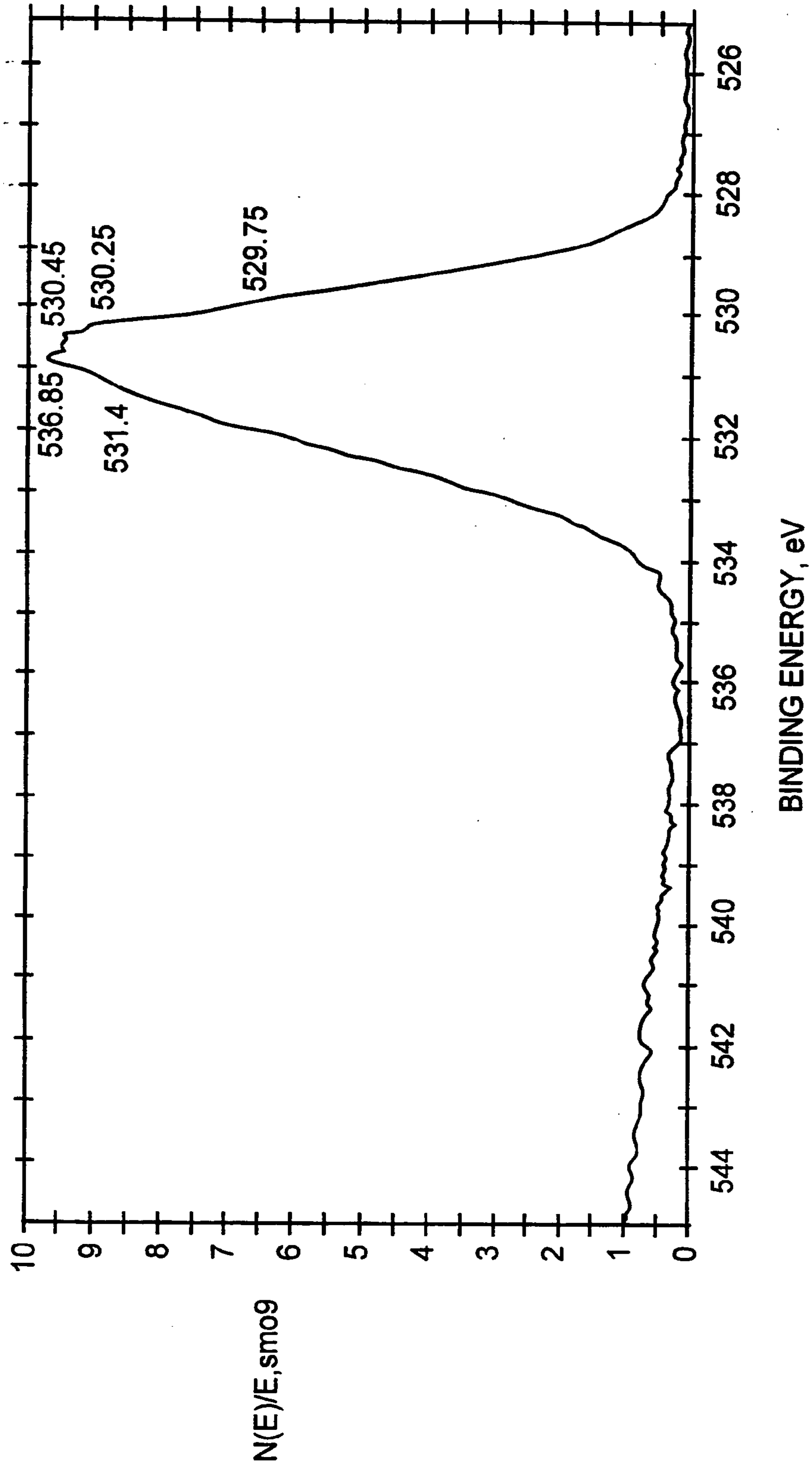

529.4
531.3
N(E)/E,smo9
10
9
8
7
6
5
4
3
2
1
0
526
528
530
532
534
536
538
540
542
544
BINDING ENERGY, eV

FIG. 4a


530.45
530.25
529.75
536.85
531.4
526
528
530
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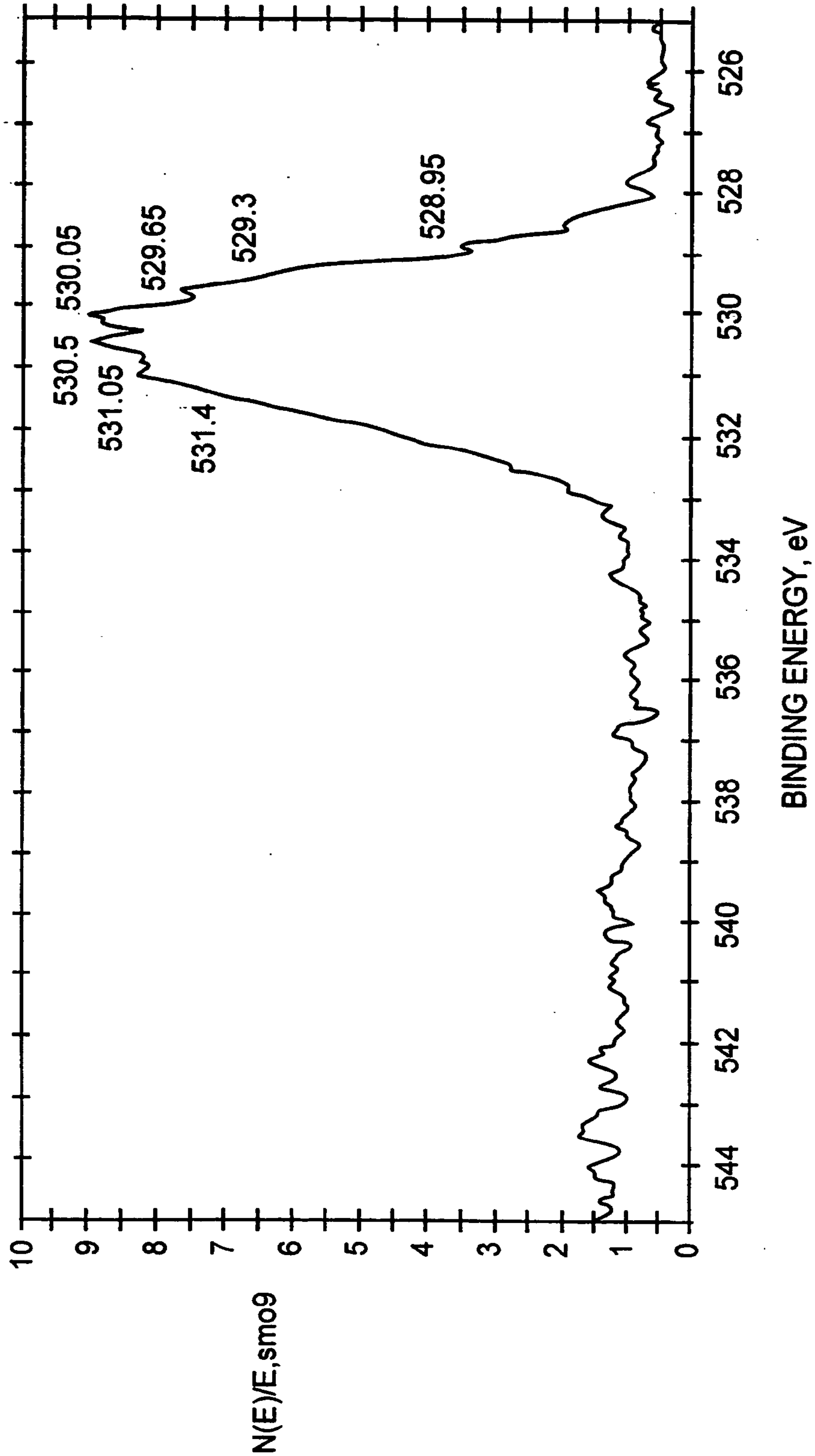
534
536
538
540
542
544
BINDING ENERGY, eV
10
9
8
7
6
5
4
3
2
1
0
N(E)/E,smo9

FIG. 4b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531.05
531.4
529.65
529.3
528.95
526
528
530
532
534
536
538
540
542
544
BINDING ENERGY, eV
10
9
8
7
6
5
4
3
2
1
0
N(E)/E,smo9

FIG. 4c

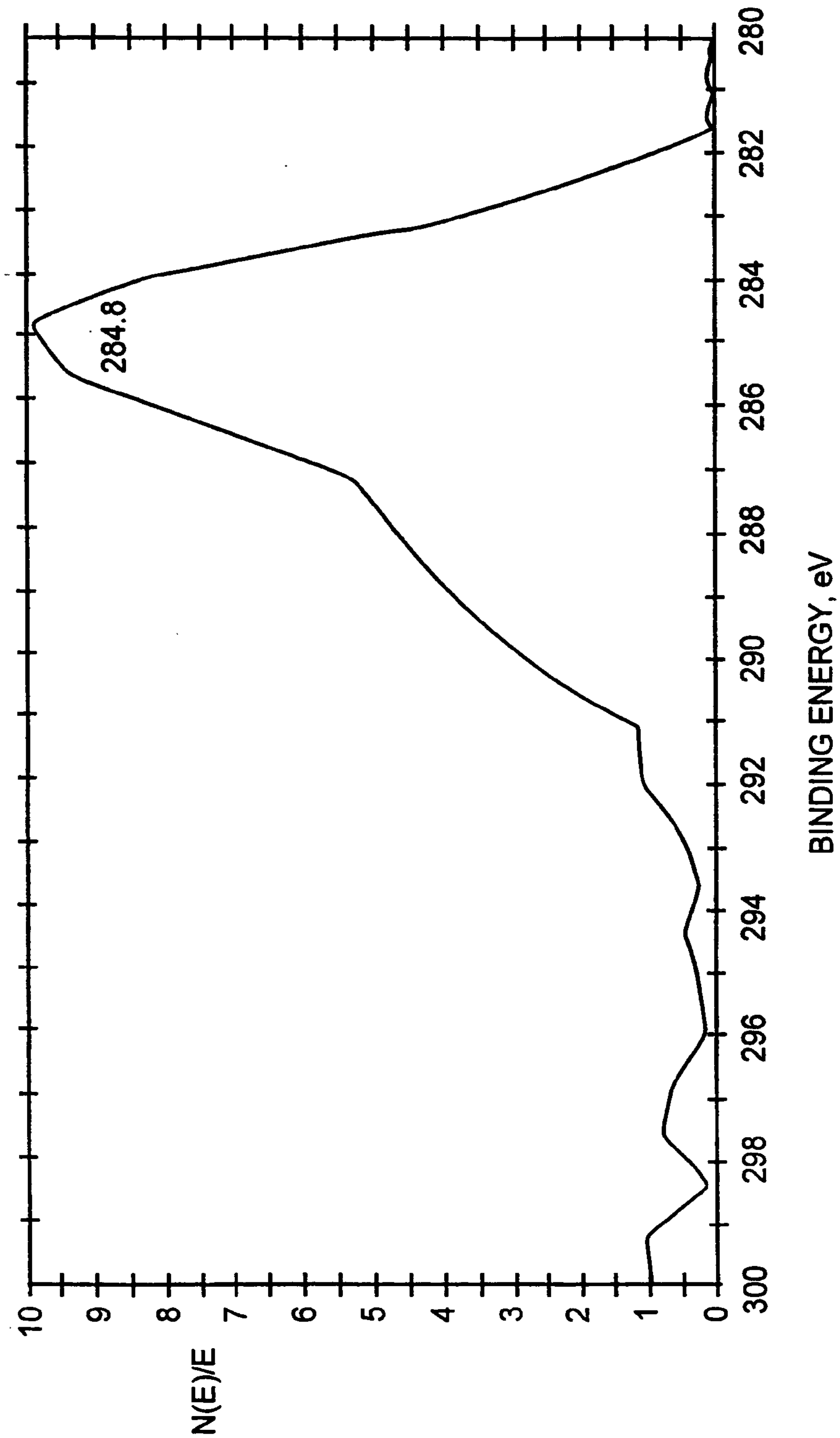
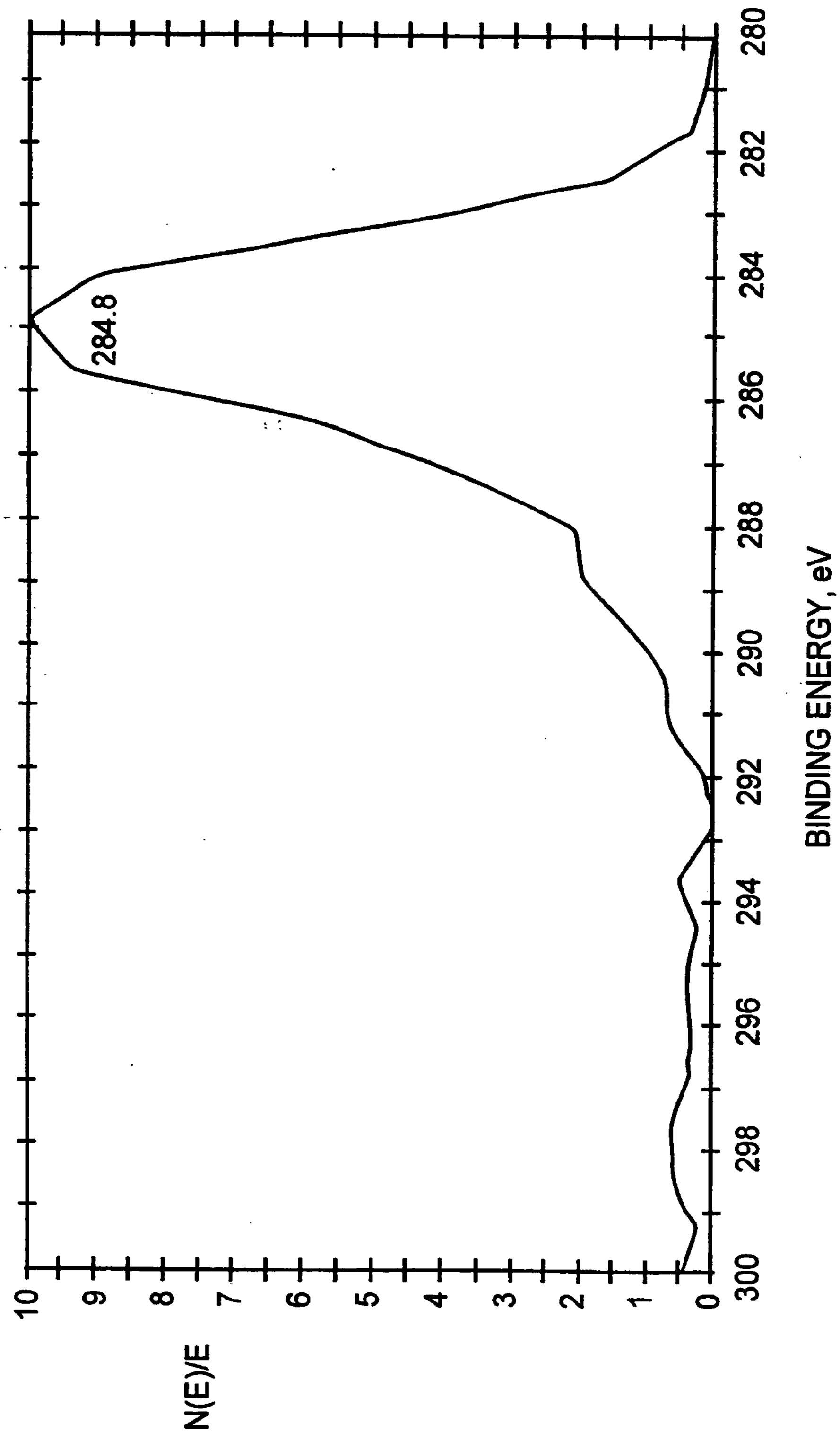

N(E)/E
10
9
8
7
6
5
4
3
2
1
0
280
282
284
286
288
290
292
294
296
298
300
284.8
BINDING ENERGY, eV

FIG. 5a


284.8
N(E)/E
10
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8
7
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5
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3
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1
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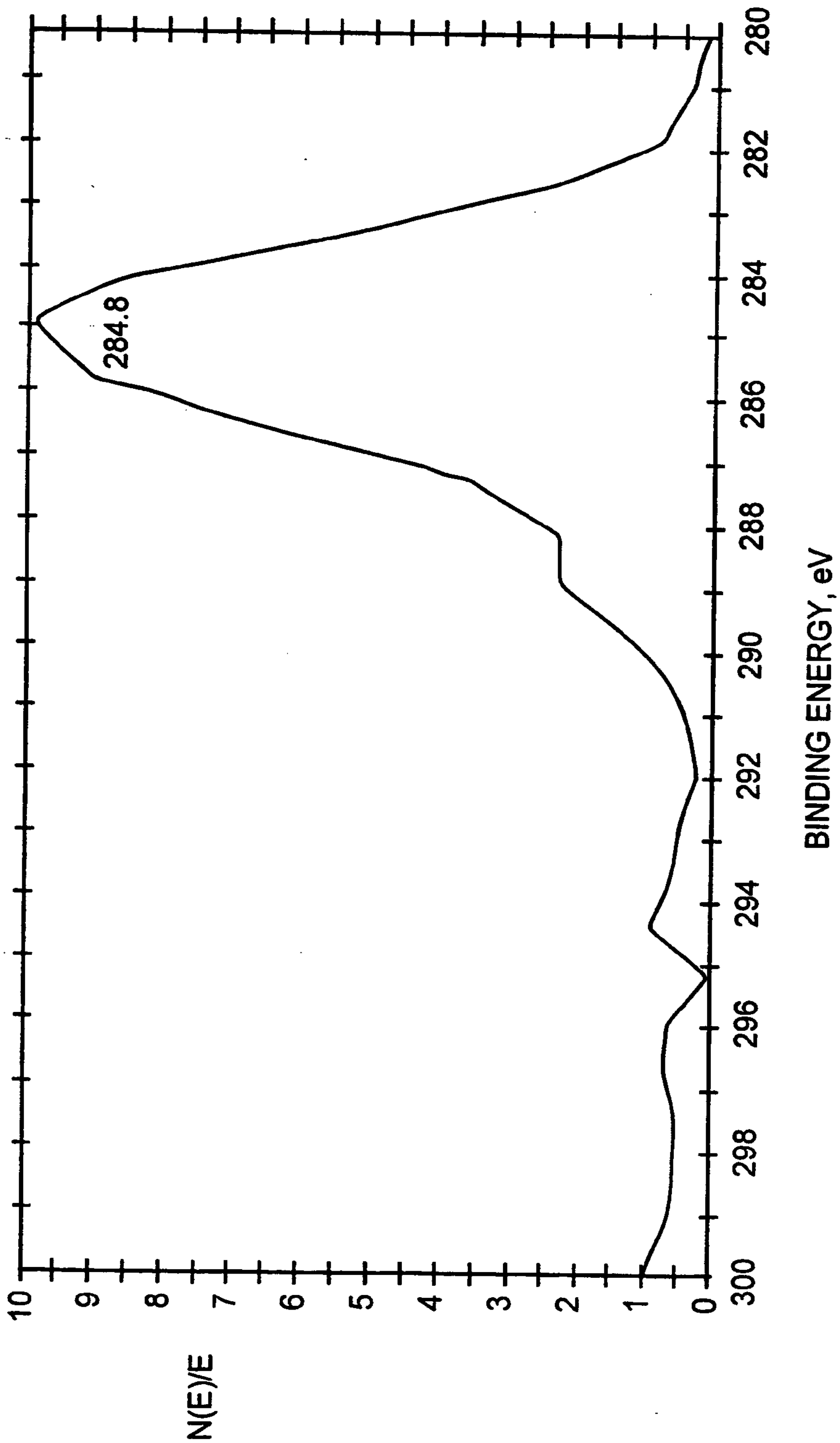
BINDING ENERGY, eV
280
282
284
286
288
290
292
294
296
298
300

FIG. 5b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N(E)/E
BINDING ENERGY, eV
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280
282
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294
296
298
300

FIG. 5C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/14064

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C14/08 C03C17/34 G02B1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,1 005 867 (PHYSIKALISCHES UNTERSUCHUNGSLABORATORIUM) 16 April 1952 see page 1, right-hand column; claims 1-10 ---	1-3,5,13
X	DE,A,34 34 583 (OLYMPUS OPTICAL CO) 11 April 1985 see examples 3,4	1,2,5,13
A	 ---	18,20
X	FR,A,2 293 719 (LEYBOLD HERAEUS GMBH & CO KG) 2 July 1976 see figure; examples 1,2	1,5,13
A	see page 4, line 1 - line 15 ---	2,3,18
A	WO,A,93 04993 (VIRATEC THIN FILMS INC) 18 March 1993 see page 29, line 25 - page 30, line 27 -----	1,5,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
9 December 1996	20. 12. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Patterson, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/14064

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		JP-A-	60064301	12-04-85
		US-A-	4599272	08-07-86
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		CA-A-	2116855	18-03-93
		EP-A-	0602153	22-06-94
		JP-T-	6510382	17-11-94

Form PCT/ISA/210 (patent family annex) (July 1992)